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Treatment of Lignin Wastewater Using Peroxydisulfate Combined with Manganese Oxide-Loaded Biochar

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Abstract

The pulp and paper industry wastewater discharge into public water, it will cause water pollution problems. In this research, lignin contaminated synthetic wastewater with a COD value of 2,401 mg/L, and color intensity of 5,432 ADMI was treated using 150 mM sodium peroxydisulfate in combination with MnO_x-loaded biochar (MnO_x-B). The MnO_x-B was produced by pyrolyzing corn core at 400 °C for 4 hours without oxygen, then dipped in 40 mM manganese sulfate for 2 hours, and heated at 600°C for 30 min without oxygen. From the characterization of MnO_x-B, the surface area, pore volume, pore size, and pH value at the zero-point charges of MnO_x-B were 153 m^2/g, 0.054 cm^3/g, 1.11 nm, and 7.23, respectively. From the FTIR spectrogram, the peak assigned to Mn-O was observed. By applying 150 mM sodium peroxydisulfate and varying three parameters: MnO_x-B dosage, initial wastewater pH, and reaction time, to treat lignin wastewater, the optimum experimental condition was obtained using 2 mg/L of MnO_x-B, under pH of 8 for 45 min. The COD and color removal efficiencies were 73% and 90%, respectively. However, the quality of the treated wastewater did not yet pass the pulp and paper mills effluent standards of the Department of Industrial Works.

Keywords: Biochar; Lignin; Manganese oxide; Oxidation; Sodium peroxydisulfate

1. Introduction

The pulp and paper industry is essential to the country's economic sector. The volume of production and exports increases every year, resulting in a large amount of income coming into the country. The paper industry is a continuation of the agricultural sector. The raw material of paper production is wood pulp. Products from the paper industry are passed on to the printing and packaging industry. Statistics from the Department of Industrial Works in 2020 indicated that Thailand had 1,616 registered factories in the pulp and paper industry (Department of Industrial Works, 2020). The pulp and paper industry consumes a large amount of water which causes water pollution. In the production process, high COD wastewater is released due to lignin. Lignin-contaminated wastewater is dark brown, creates an unsightly view, obstructs light transmission underwater, inhibits photosynthesis, and reduces the DO value in water (Pokhrel and Viraraghavan, 2004). If lignin in wastewater is left untreated for a long time, it is decomposed into phenols, aldehydes, ketones, methanol, and carboxylic acids, which are harmful to the ecosystem (Asina *et al.,* 2016).

There are several methods of lignin treatment. Biotechnology (Haq *et al.,* 2020; Asina *et al.,* 2017) is a possible method, but it takes a long time to treat. The coagulation-flocculation process is a physicochemical process in which aluminum chloride, alum, chitosan, or polyaluminum chloride (PACl) is added to wastewater to precipitate contaminants (Kamali and Khodaparast, 2015; Lee *et al.,* 2014; Renault *et al.,* 2009; Lindholm-Lehto *et al.,* 2015).

However, the production of a large amount of sludge by this method is a problem that must be further solved. Adsorption is also widely applied (Andersson *et al.,* 2012), but the adsorption efficiency is limited, and the method requires an additional step to separate the adsorbent from wastewater. The advanced oxidation process can oxidize recalcitrant organic pollutants (Covinich *et al.,* 2014) to carbon dioxide and water or less toxic organic matter. The most widely used chemicals are ozone, hydrogen peroxide, chlorine, permanganate, and Fenton's reagent (Riadi *et al.,* 2019; Nominoya *et al.,* 2013; Wang *et al.,* 2015). Researchers used sulfate radicals to oxidize organic matter in wastewater and reported that sulfate radicals were more effective at oxidizing than other chemicals. Peroxydisulfate has a higher redox potential than peroxymonosulfate (Bard *et al.* 1985; Spiro 1979); peroxydisulfate therefore tends to have a higher treatment efficiency. Researchers used persulfate activation to form radical sulfate to increase the oxidizing efficiency. There are several activation methods, including heat, metal oxides (such as aluminum oxide, nickel oxide, zero-valent ion, manganese oxide, titanium oxide, and cerium oxide) (Hua *et al.,* 2012; Ghanbari *et al.,* 2017; Matzek and Carter, 2016; Aher *et al.,* 2017), UV, and alkali. Among all processes, metal oxides are most commonly used. Manganese oxide is readily available naturally and cheaply. Moreover, the excellent properties of manganese oxide, such as its various Mn valences and low toxicity, make it interesting for use as a catalyst (Jia *et al.,* 2021). Carbon-based materials, including activated carbon, carbon nanotubes, and biochar, can also activate persulfate (Zhao *et al.,* 2017). Carbon-based materials act as electron donors for persulfate so that sulfate radical formation can occur. The biochar modified with manganese oxide was successfully applied to increase the persulfate oxidation efficiency (Fan *et al.,* 2019). In addition to being used as catalysts, manganese oxide and biochar were also employed to absorb pollutants. Faheem *et al.* (2016) increased water pollution adsorption efficiency using manganese oxide-loaded biochar.

As mentioned above, manganese oxide-loaded biochar was used for different purposes, but studies on the effects of simultaneous wastewater treatment with more than one mechanism are limited. The researcher was interested in studying the influence of manganese oxide-loaded biochar on the simultaneous adsorption and oxidation processes. This study investigated lignin-contaminated wastewater's treatment efficiency using peroxydisulfate and co-treatment with biochar from corn cores enhanced with manganese oxide. Various factors affecting the treatment, including the initial pH of wastewater, MnO_x-B dosage, and reaction time, were observed. The kinetic study was included.

2. Materials and Methods

2.1 Preparation of synthetic wastewater contaminated with lignin

Lignin purchased from Sigma-Aldrich (1.5 g) was dissolved in 1,000 mL of double-distilled water. The solution was analyzed for COD concentration by closed reflux method and color by UV-Visible Spectrophotometer (280 nm).

2.2 Biochar (B) and Biochar enhanced with manganese oxide (MnO_x-B) preparation (Modified from Fan et al., 2019)

Corn core was washed with clean water, cut into small pieces, oven-dried at 100 °C for 24 hours, and passed through the pyrolysis process at 400 °C for 4 hours without oxygen. The produced biochar (B) was then ground and passed through a 35-mesh sieve. Biochar enhanced with manganese oxide (MnO_x-B) was produced by adding 20 g of powder biochar to 1 L of 40 mM manganese sulfate solution. The solution was stirred at 120 rpm for 2 hours, filtered, oven-dried at 100 °C for 24 hours, further heated at 600 °C for 30 min without oxygen, washed with deionized water, and oven-dried at 60 °C for 24 hours.

2.3 Biochar (B) and Biochar enhanced with manganese oxide (MnO_x-B) characterization

The surface structural groups of B and MnO_x-B were characterized using a Fourier Transform Infrared Spectrometer with

KBr pellet sample preparation technique (FTIR; Perkin Elmer model spectrum GX). Brunauer Emmett Teller (BET)/Gas Adsorption Analyser analyzed the surface area, pore volume, and pore size. The Mn composition in B and MnO_x-B were determined using Acid digestion/Atomic Absorption Spectrophotometer (US. EPA: SW-846 Method 3050b, 1996). The pH value at the zero-point charges of MnO_x-B was determined by preparing the 0.01 M NaCl solution at various pHs, adding an adsorbent, measuring the solution pH after shaking for 24 hours, and plotting the graph between the initial and final pH (Ahmed *et al.,* 2016).

2.4 Oxidation experiments

A required amount of MnO_x-B was added to 50 mL synthetic wastewater containing 150 mM sodium peroxydisulfate. The pH was adjusted by 0.1 M HCl or 0.1 M NaOH. The solution was stirred at 120 rpm for various periods and then filtered through 0.42-µm filter paper. After treatment, the COD and color of solutions were determined. Degradation kinetics was calculated following the pseudo-first-order kinetic model:

$$ln\left(\frac{C_t}{C_0}\right) = -k_1 t$$

C_t = the COD concentration or color intensity in solution at time t (mg/L or ADMI)

C_0 = the COD concentration or color intensity in solution at time 0 (mg/L or ADMI)

t = time (min)

k_1 = the rate constant for pseudo-first order adsorption (1/min)

2.5 Adsorption experiments

The batch process experiment was carried out by adding MnO_x-B to 50 mL of synthetic wastewater. The pH was adjusted. The solution was stirred at 120 rpm for various periods and then filtered through 0.42-µm filter paper. After treatment, the COD and color of solutions were determined. Adsorption kinetics was calculated using the equations below.

The pseudo-first order $log(q_e - q_t) = logq_e - k_1 \frac{t}{2.303}$

The pseudo-second order $\frac{t}{q_t} = \frac{1}{k_2 q_e{}^2} + \frac{t}{q_e}$

q_t = the amount of adsorbed substance per unit mass of adsorbent at time t (mg/g)

q_e = the amount of adsorbed substance per unit mass of adsorbent at equilibrium (mg/g)

t = time (min)

k_1 = the rate constant for pseudo-first order adsorption (1/min)

k_2 = the rate constant for pseudo-second order adsorption (g/mg.min)

2.6 Statistical analysis

All experiments were triplicated and calculated the average value. A standard deviation calculation observed an experimental precision. The data difference within and between the test set at a 95% confidence level was tested using SPSS version 26 (one-way analysis of variance; ANOVA).

3. Results and Discussion

3.1 Wastewater characteristics

Synthetic wastewater's pH, COD, and color values were 8, 2,401 mg/L, and 5,432 ADMI. After adding the biochar and sodium peroxydisulfate, the pH of the wastewater changed to 2.48.

3.2 Biochar (B) and Biochar enhanced with manganese oxide (MnO_x-B) characteristics

After enhanced biochar with manganese oxide, the surface area was increased (Table 1). However, the pore size and total pore volume were decreased due to the deposition of manganese oxide on the biochar surface.

For biochar, the band at 3270 cm^{-1} corresponded to the stretching vibration of hydroxyl functional groups, while the band appearing at 1014 cm^{-1} could be assigned to the C-O stretching vibration. The band at 1610 cm^{-1} represented the C = O stretching vibration of the -COOH group.

Functional groups such as C-OH and -COOH transformed into CO˚ and COO˚ and activated persulfate to generate sulfate free radicals (Fan *et al.,* 2019). The bands at 1610 and 1014 cm−1 decreased after modifying biochar with manganese oxide due to the heating process at 600 ˚C for 30 min. High heat increased the degradation of cellulose and hemicellulose. The peak around 600 cm^{-1} was assigned to Mn-O appeared in MnO_x-B. The confirmation of Mn presenting on the MnO_x-B surface was by AAS determination. The Mn concentration in B and MnO_x-B were 0.001 mg/g and 1.083 mg/g, respectively. The pH at the point of zero charges of MnO_x-B was 7.23.

3.3 Effect of initial pH

In the oxidation process, 1 g of MnO_x-B was added to 50 mL synthetic wastewater containing 150 mM peroxydisulfate. The solution pH was adjusted using 0.1M HCl or 0.1 M NaOH. The reaction time was 60 min. The initial pH of synthetic wastewater was 8, close to real wastewater (7.9). Adding MnO_x-B to wastewater, the solution pH did not change. When adding peroxydisulfate to wastewater, the pH decreases due to water being oxidized (four-electron oxidation) into oxygen and hydrogen ions, as shown in equation 1 (Lee *et al.,* 2018).

$$2S_2O_8^{2-} + 2H_2O \longrightarrow 4SO_4^{2-} + O_2 + 4H^+ \quad (1)$$

Moreover, the homolytic fission of the O-O bond of peroxydisulfate occurred. The sulfate radical anions ($SO_4^{\circ-}$), hydroxyl radical ($^{\circ}OH$), and hydrogen ion (H^+) were formed, as shown in equations 2 and 3.

$$S_2O_8^{2-} \longrightarrow 2SO_4^{\circ-} \quad (2)$$

$$SO_4^{\circ-} + H_2O \longrightarrow SO_4^{2-} + {}^{\circ}OH + H^+ \quad (3)$$

From Figure 2, when adjusting the pH of the initial wastewater to 3, the percentage of COD and color removal was 65% and 81% due to the effect of peroxydisulfate and MnO_x-B (equations 4-9). When the wastewater was adjusted to have a higher pH value, COD and color removal efficiency were only slightly increased. The increase might be due to the acceleration of water oxidation to $^{\circ}OH$, SO_5^{2-}, and HO_2^- in alkaline solution (equations 10 to 12).

Table 1. Results from Brunauer Emmett Teller (BET)/Gas **Adsorption Analyser**

	B	*MnO_x-B*
BET surface area (m^2/g)	97	153
Pore size (nm)	1.62	1.11
Total pore volume (cm^3/g)	0.082	0.054

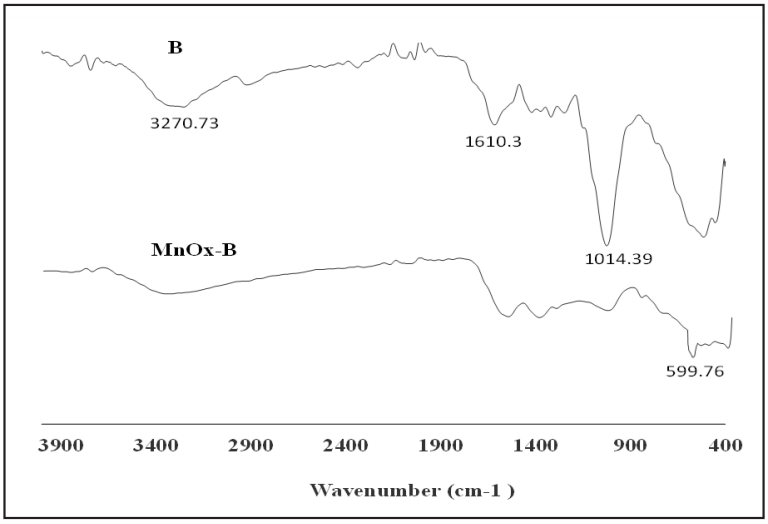

Figure 1. FTIR spectrogram of Biochar (B) and Biochar enhanced with manganese oxide (MnO_x-B)

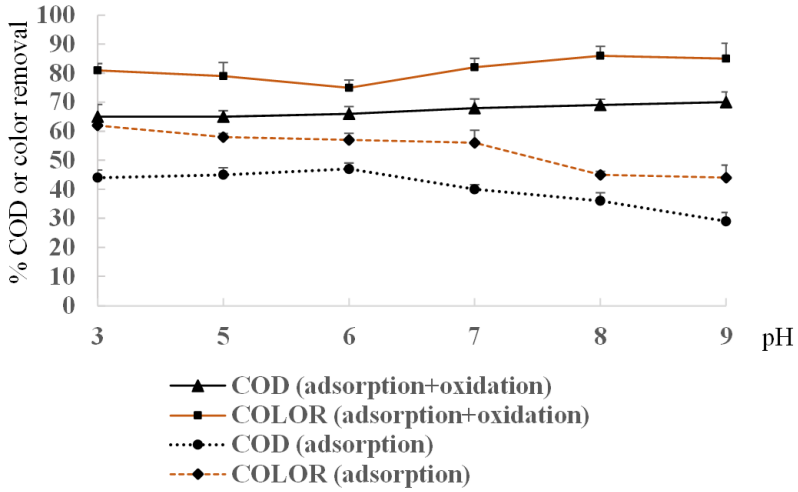

Figure 2. COD and color removal percentage using different pH.

In an oxidation process without a catalyst, equations 4-6 could occur.

$$S_2O_8^{2-} + {}^{\circ}OH \longrightarrow SO_4^{\circ-} + HSO_4^- + 1/2O_2 \quad (4)$$
$$S_2O_8^{2-} + {}^{\circ}OH \longrightarrow S_2O_8^{\circ-} + OH^- \quad (5)$$
$$S_2O_8^{2-} + SO_4^{\circ-} \longrightarrow S_2O_8^{\circ-} + SO_4^{2-} \quad (6)$$

Equations 7 and 8 represented occurring continuous reactions.

$$S_2O_8^{2-} + HO_2^- \longrightarrow SO_4^{\circ-} + SO_4^{2-} + O_2^{\circ-} + H^+ \quad (7)$$
$$S_2O_8^{2-} + O_2^{\circ-} \longrightarrow SO_4^{\circ-} + SO_4^{2-} + O_2 \quad (8)$$

Applying MnOx-B as a catalyst, the reaction could be as in equation 9.

$$M^{n+} + S_2O_8^{2-} \longrightarrow M^{(n+1)+} + SO_4^{\circ-} + SO_4^{2-} \quad (9)$$
$$SO_4^{\circ-} + OH^- \longrightarrow SO_4^{2-} + {}^{\circ}OH \quad (10)$$
$$S_2O_8^{2-} + OH^- \longrightarrow SO_5^{2-} + SO_4^{2-} + H^+ \quad (11)$$
$$SO_5^{2-} + OH^- \longrightarrow HO_2^- + SO_4^{2-} \quad (12)$$

In the case of increasing pH and adding heavy metals as a catalyst, the metal ions are hydrolyzed to form their hydroxy complexes that are stronger electron donors than the uncomplexed species. As in Figure 2, the treatment efficiency was not statistically different at a 95% confidence level when the initial pH was adjusted to 8 and 9.

In the adsorption process, one gram of MnOx-B was added to 50 mL of synthetic wastewater without peroxydisulfate. The pH was adjusted using 0.1M HCl or 0.1 M NaOH. The reaction time was 60 min. The COD and color removal efficiency was low in the basic solution. The pH of 7.23 was the pH at which the net charge of the total MnO_x-B surface was equal to zero. At pH higher than 7.23, the surface charge of MnO_x-B became negative. The negatively charged surface of MnO_x-B repelled anionic lignin, thus lowering the adsorption yield.

3.4 Effect of dosage

The oxidation was performed using 150 mM peroxydisulfate at pH 8 for 60 min. From Figure 3, the efficiency of wastewater treatment when adding 2 g of MnO_x-B was better than when adding 1 g. However, in the case of adding more MnO_x-B, it did not significantly increase the efficiency of wastewater treatment at the 95% confidence level. Adding more than 2 g of the catalyst could not enhance treatment efficiency but may increase the reaction rate. However, the reaction rate was not studied when using a catalyst greater than 2 g.

The adsorption was also carried out at pH 8 for 60 min. The results indicated that the more MnO_x-B added, the more adsorption would occur. Increasing MnO_x-B dosage could increase the adsorption surface area.

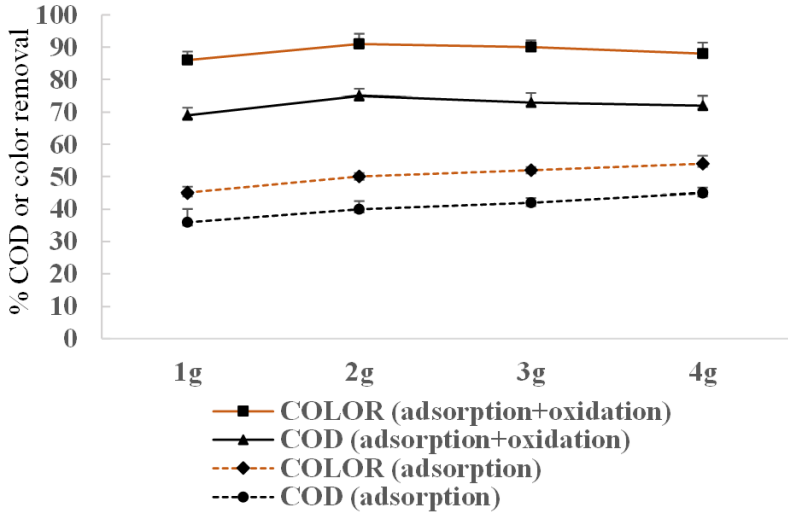

Figure 3. COD and color removal percentage using different dosage.

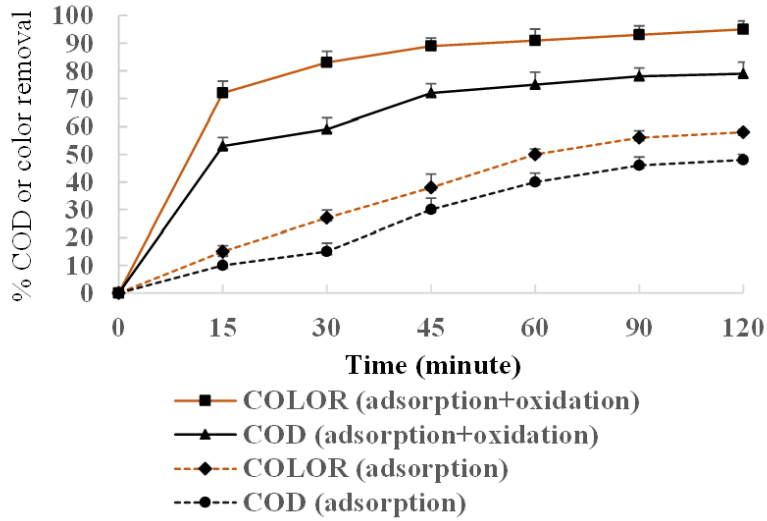

Figure 4. COD and color removal percentage using different reaction times

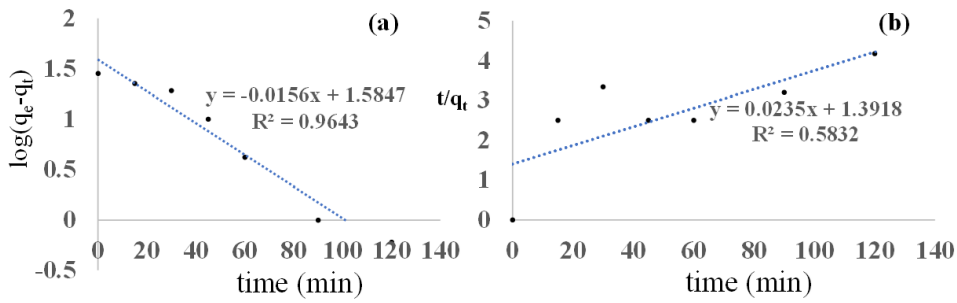

Figure 5. Pseudo-first order (a) and Pseudo-second order (b) kinetic model for adsorption process

3.5 Effect of reaction time

Figure 4 showed the results of wastewater oxidation by 150 mM peroxydisulfate combined with 2 g MnO_x-B at pH 8. During the first 15 min, the slope of both COD and color treatment curves was high. The *k* value for COD and color removal were 0.0503 min^{-1} and 0.0849 min^{-1}. After 15 min, the treatment was at a lower rate. The *k* value for COD and color removal were 0.0172 min^{-1} and 0.0311 min^{-1}. When reaction times were 45, 60, 90, and 120 min, the treatment efficiency was not significantly different at a 95% confidence level. For the adsorption process, the rate of treatment was slower than the oxidation process. The adsorption yield was slowly increased. The adsorption equilibrium was reached within 90 min. From Figure 5, the best-fitting kinetic model for lignin was the pseudo-first-order kinetic with the R^2 value of 0.9643 and *k* value of 0.0359 min^{-1}.

When the optimal condition was applied for wastewater treatment with peroxydisulfate combined with MnO_x, the value of COD and color were reduced to 528.28 mg/L and 488.91ADMI. According to the pulp mill effluent standard, the COD and color must not exceed 400 mg/L and 600 ADMI. The COD and color of paper factory effluent must not exceed 270 mg/L and 350 ADMI (Ministry of Natural Resources and Environment, 2018). The COD of the treated wastewater in this study did not yet pass the effluent control standards of the Department of Industrial Works for pulp and paper mills. If the pH of the wastewater is adjusted to become more acidic after the oxidation process, it may be possible to increase the adsorption process, and therefore, the treatment efficiency may be higher. Residual sulfate in wastewater is another issue that must be considered and studied further. Sulfate must be treated using an appropriate technique such as lime precipitation before discharge into the environment.

4. Conclusion

This research confirmed that the combined use of MnO_x-B in peroxydisulfate oxidation contributes to enhance color and COD treatment efficiency. The higher the pH, the higher the overall treatment efficiency. The adsorption process was poor as the pH value was unsuitable for this process. Increasing MnO_x-B dosage could increase the adsorption. The quality of the treated wastewater did not yet pass the effluent control standards of the Department of Industrial Works for pulp and paper mills.

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